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An optically transparent thin-layer electrochemical cell for the study of vibrational circular dichroism of chiral redox-active molecules

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An optically transparent thin-layer electrochemical (OTTLE) cell with a locally extended optical path has been developed in order to perform vibrational circular dichroism (VCD) spectroscopy on chiral molecules prepared in specific oxidation states by means of electrochemical reduction or oxidation. The new design of the electrochemical cell successfully addresses the technical challenges involved in achieving sufficient infrared absorption. The VCD-OTTLE cell proves to be a valuable tool for the investigation of chiral redox-active molecules. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4793722>]

I. INTRODUCTION

Electrochemical cells that enable secondary chemical reactions to be monitored *in situ* under controlled conditions (e.g., temperature, pressure) are very useful for the selective detection, identification and characterization of short-lived redox species and detailed investigation of redox paths.¹ Chiral molecules that exhibit distinct chiroptical signatures upon electrochemical generation of radical ions in solution are generally investigated with electronic circular dichroism (ECD) spectroscopy.²⁻⁴ The high ECD signal intensities generally observed for organic or inorganic compounds make circular dichroism (CD) spectroelectrochemistry a suitable tool to determine chiroptical and stereochemical properties of natural and synthetic optically active compounds. *In situ* ECD spectra of electrochemically generated target species have appeared in several reports on chiroptical activity of redox-active molecular systems in the UV-Vis spectral region.²⁻⁴ However, such studies are limited to species featuring an optically active chromophore.

CD associated with vibrational transitions, also known as vibrational circular dichroism (VCD),^{5,6} provides much more structural information, and has emerged as one of the most powerful spectroscopic techniques to determine the absolute configuration and conformation of chiral molecules in solution.^{7,8} Consequently, VCD has become an essential tool employed in biophysical, biochemical, and pharmaceutical research laboratories.⁹⁻¹⁶ To the best of our knowledge, the only VCD spectra of chiral organic radicals have been reported by Mori *et al.*¹⁷ However, these radical cations were obtained on addition of a chemical oxidant, so that many aspects of the chiroptical activity (e.g., the reversibility of the oxidation, and possible intermediate states) could not be investigated. Here we report the first practical design of an

optically transparent thin-layer electrochemical (OTTLE)¹⁸ cell applicable for VCD measurements on electrochemically generated radical ions, using a commercially available VCD spectrometer.

II. PRACTICAL CONSIDERATIONS FOR SPECTROELECTROCHEMICAL MEASUREMENTS

The combination of thin-layer cyclic voltammetry (TL-CV) and spectroelectrochemistry (SEC)¹ involves practical challenges that need to be addressed. Acquiring acceptable mid-infrared absorption spectra of redox active species requires combination of an appropriate window material (e.g., CaF₂, BaF₂, NaCl, KBr, CsI), supporting electrolyte and aprotic solvent (e.g., acetonitrile, dichloromethane, tetrahydrofuran, including their deuterated forms) to create wide transparent spectral windows in the functional-group, fingerprint, and aromatic regions showing characteristic vibrational modes of the redox pairs. Often, target compounds require highly concentrated solutions in order to obtain sufficiently high optical density (≈ 1 OD) for a VCD measurement. Working with highly concentrated solutions (> 10 mM) may lead to complications such as formation of aggregates and irreversible chemical processes. Moreover, the combination of long measurement times (required to obtain a good VCD spectrum) and concentrated samples requires a balanced design for an optimum performance of the cell. For any design of the OTTLE¹⁸ construction, the thickness of the electrolyte layer around the working electrode is a key geometrical detail that determines the electrolysis time.¹

III. VCD SPECTROELECTROCHEMICAL CELL

Introducing a more sophisticated design of the working electrode to meet the practical requirements of a VCD measurement inevitably compromises the time for electrolysis to be completed. We have therefore adapted an OTTLE cell¹⁸

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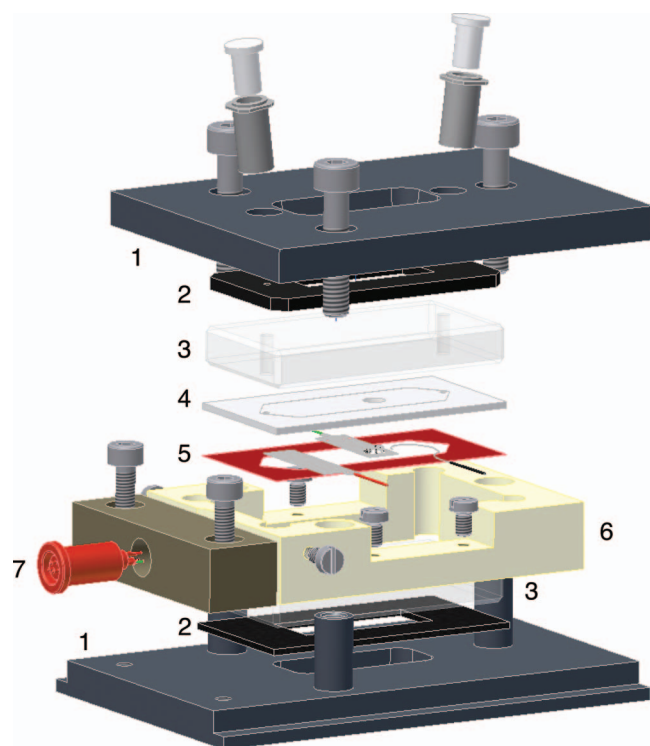


FIG. 1. Exploded view of the VCD-OTTLE cell: 1. metal cover plates (with filling ports); 2. rubber gasket; 3. CaF₂ window; 4. custom polytetrafluoroethylene (PTFE) spacer (1 mm thick) with a circular aperture (4 mm diameter); 5. custom polyethylene-electrode spacer (see enhanced view in Fig. 2); 6. protective frame; 7. electrode plug.

by introducing a relatively long pathlength (1.2 mm) in the probed area, which is customized to efficiently perform VCD measurements. Details of the cell construction are shown in Fig. 1.

The new construction contains two principal modifications: (a) a new non-planar shape of the working electrode melt-sealed into the polyethylene spacer together with the counter and pseudo-reference electrodes, and (b) addition of an extra polytetrafluoroethylene (PTFE) spacer with a customized geometry (see Fig. 2). In particular, a small cut has been made in the centre of the 5 × 6 mm Pt minigrid, and the cut wires have been folded outwards, resulting in a cylindrical protrusion in the centre of the working electrode and introducing a 3.5 mm-diameter hole in the centre of the Pt minigrid (see Fig. 2). A 1 mm thick PTFE spacer with a circular aperture of 4 mm diameter facing the Pt minigrid aperture (Fig. 2) is placed on top of the 0.2 mm PE spacer with melt-sealed electrodes. The PTFE spacer has four major functions: it (1) maintains the cylindrical shape of the working electrode when the upper CaF₂ window is put in place; (2) preserves the thin-layer geometry at the counter and pseudo-reference electrodes in order to avoid diffusion of products from the working electrode; (3) allows for a large volume of solution only at the probing site so as to increase the optical pathlength; (4) serves as a mask for the remaining thin-layer area of the electrode compartment. The total 1.2 mm optical pathlength ensures sufficient infrared absorption intensity to measure VCD signals on solutions with concentrations as low as 7×10^{-3} mol dm⁻³. The pro-

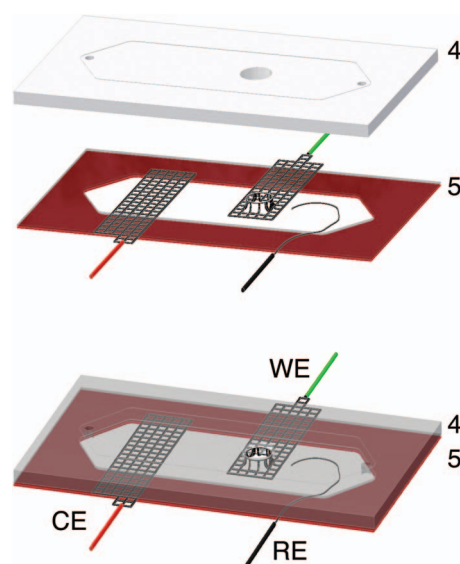


FIG. 2. Enhanced view of the PTFE spacer and the custom polyethylene-electrode spacer. WE: working electrode (shaped Pt minigrid), CE: counter electrode (flat Pt minigrid), RE: pseudoreference electrode (Ag wire).

truding cylindrical shape of the minigrid electrode ensures a complete, although relatively slow (≈ 3 min), electrochemical conversion along the whole optical path. Figure 3 shows the reversible cyclic voltammogram of 7×10^{-3} M of (S)-methyl 2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoate in CD₃CN (0.1 M Bu₄NPF₆) recorded at the scan rate of 5 mV s^{-1} .

The color change of this compound upon reduction can be used conveniently to assess whether the redox-active species is actually converted in the whole cylindrical volume at the probing site. In Fig. 4 we show photographs of the VCD-OTTLE cell containing the solution of the test compound. Upon electrochemical reduction, the colorless parent compound is completely converted to the yellow-green radical anion inside the cylindrical probing volume. The completion and reversibility of the electrolysis has been confirmed by isosbestic UV-Vis spectral changes (see Ref. 19). The completion of the electrolysis in the cylindrical space is probably due to charge migration in the electric field. Importantly, the same remarkable effect, i.e., completed electrolysis, is observed for an exclusively thin-layer configuration of the electrode compartment, when the Pt minigrid working electrode features a 2-mm circular hole in the center. No electrolysis takes place at this distance from the outer edges of the working electrode.

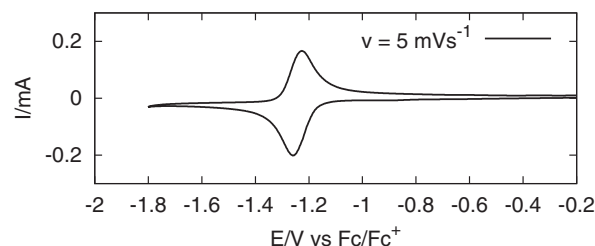


FIG. 3. CV of (S)-methyl 2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoate in CD₃CN (0.1 M Bu₄NPF₆) recorded at the scan rate of 5 mV s^{-1} with a PA4 potentiostat (EKOM, Połna, Czech Republic).

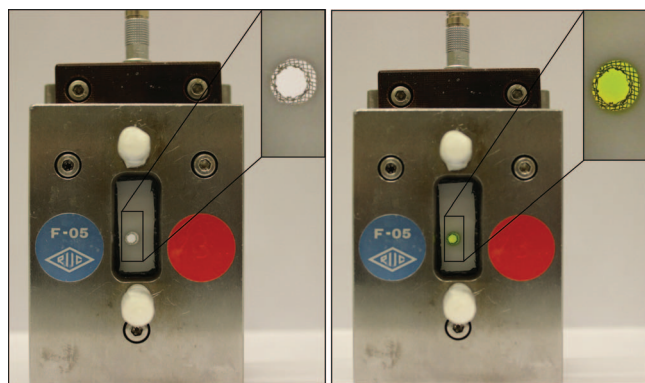


FIG. 4. Pictures of the VCD-OTTLE cell containing the neutral (left) and radical anion (right) forms of (S)-methyl 2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoate in CD_3CN (0.1 M Bu_4NPF_6). Inset: closeup of the cylindrical probing volume before and after the complete electrolysis.

IV. VCD-SPECTROELECTROCHEMICAL ASSEMBLY

The spectroelectrochemical VCD measurements were performed using a Bruker PMA 50 VCD module in combination with a Bruker Vertex 70 FTIR spectrometer. The new design of the OTTLE cell required adaptation of the PMA 50 sample compartment, since the resulting small aperture in the PTFE spacer would otherwise cause significant clipping of the circularly-polarized infrared light. We therefore assembled an optical (Kepler) telescope in the sample compartment, consisting of two ZnSe lenses of 50 and 38 mm focal lengths (see Fig. 5). The telescope allows the circularly-polarized infrared beam to focus into the small volume of solution where the electrochemical conversion occurs. The 3-mm beam waist is sufficiently small for all the infrared light to be transmitted through the 3.5-mm diameter hole in the grid of the working electrode.

V. VCD SPECTRA OF *IN SITU* ELECTROGENERATED RADICALS

A typical measurement performed with the VCD-OTTLE is shown in Fig. 6, in which displays the previously re-

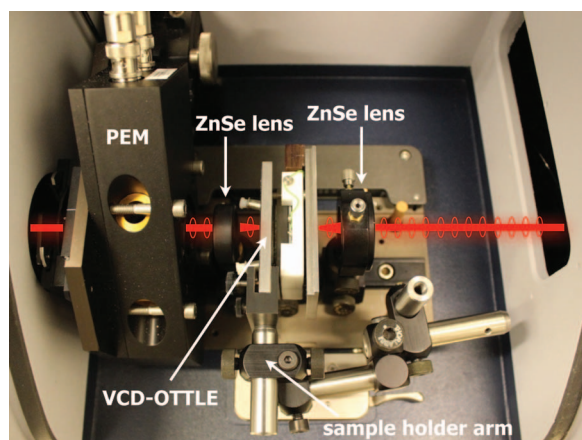


FIG. 5. Adapted PMA50 sample compartment where the VCD-OTTLE cell is fixed in a sample holder arm between the two ZnSe lenses ($f = 50$ and 38 mm; PEM = Photoelastic modulator).

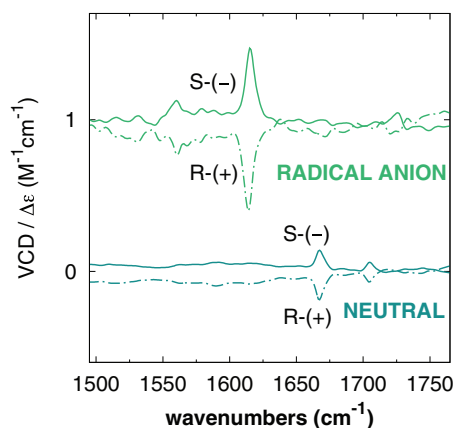


FIG. 6. VCD spectra of (R)- and (S)-methyl 2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoate and its radical anions obtained with the VCD-OTTLE cell. Reproduced by permission from Domingos *et al.*, Chem. Commun. **48**, 353–355 (2012). Copyright 2012 of The Royal Society of Chemistry.

ported VCD spectra of (R)- and (S)-methyl 2-(1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoate in their neutral and radical anionic forms. The spectra show that upon electrochemical conversion from the neutral to the radical anionic species, the CO-stretch VCD bands undergo an amplification by about one order-of-magnitude. The origin of this enhancement is described in detail elsewhere.¹⁹

VI. CONCLUDING REMARKS

We have reported on the design of an OTTLE cell that enables *in situ* measurement of VCD spectra of radicals in solution for both organic and inorganic molecular systems. VCD is increasingly employed as the technique of choice for the study of chirality in the solution phase and has become a tool of utmost importance in biophysical, biochemical, and pharmaceutical laboratories for the determination of absolute configuration. Our VCD-OTTLE cell has been developed to overcome the problems encountered due to the inherently small VCD signals. This is because in radical ions, which can be prepared in the VCD-OTTLE cell, a strong mixing of low-lying electronically excited states can lead to strong amplification of the VCD signals.¹⁹ Along with this general effect, the VCD-OTTLE cell design will be of general use by making it possible to investigate redox-active chiral compounds. Using the VCD-OTTLE cell, these compounds can be prepared in specific oxidation states in a controlled manner and simultaneously investigated with VCD, allowing for a detailed determination of their configuration and conformation.

On a more general level, this cell is also very well suited for the application of spectroscopic techniques on redox-active species where light scattering needs to be avoided. Examples include time-resolved laser spectroscopy, nonlinear optical techniques, and imaging.

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